



PATENT
Docket M 6794 HST-AUTO-CS

WATER-BASED PAINT-REMOVING SOLUTION

5 CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority from provisional application Ser. No. 60/259,667, filed January 4, 2001, incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

10 This invention relates to cleaning paint, whether fresh, dried, and/or aged, from surfaces where such paint is not desired. More particularly, this invention relates to cleaning paint from paint spraying equipment, to a novel water-based solution for accomplishing such cleaning, and to a concentrate from which the solution can be made by dilution with water only.

15 Current commercial practice in the art preponderantly utilizes solutions that comprise a component of amines and a component of organic solvent generally selected from the group consisting of simple alcohols and monoethers of glycols, most or all with molecules that contain no more than eight carbon atoms, in order to have sufficient water solubility. The amines used are typically alkanolamines like dimethyl ethanol amine, methyl isopropanol amine, and diethanol amine but are not limited to this
20 class of amines. Typical solvents used in the solution are alcohols and glycol ethers, such as n-butanol, ethylene glycol mono butyl ether, diethylene glycol n-butyl ether, triethylene glycol methyl ether, propylene glycol normal butyl ether, dipropylene glycol methyl ether, propylene glycol methyl ether, and propylene glycol normal propyl ether. Typical concentrate formulas consist of 85 to 99 % of solvent and 1 to 15 % of
25 alkanolamine, with the balance water. The concentrates are usually diluted to from 5 % to 15 %, by weight or volume, in deionized water for use as a working water-based paint-removing solution. Operating temperature when using the water-based solution is usually from 21 to 55 °C.

30 Many of the constituents of conventional paint removing solutions are legally classified as "volatile organic compounds", hereinafter usually abbreviated as "VOC". A major object of this invention is to provide paint flushing solutions and processes that are as technically satisfactory for paint flushing as current commercial processes but

have substantially lower VOC content and/or emissions. Other alternative and/or concurrent objects will become apparent from the description below.

Except in the claims and the operating examples, or where otherwise expressly indicated to the contrary, all numerical quantities in this description indicating amounts of material or conditions of reaction and/or use are to be understood as modified by the word "about" in describing the broadest scope of the invention. Practice within the numerical limits stated is generally preferred, however. Also, throughout the description and claims, unless expressly stated to the contrary: percent, "parts of", and ratio values are by weight; the term "polymer" includes "oligomer", "copolymer", "terpolymer", and the like; the description of a group or class of materials as suitable or preferred for a given purpose in connection with the invention implies that mixtures of any two or more of the members of the group or class are equally suitable or preferred; description of constituents in chemical terms refers to the constituents at the time of addition to any combination specified in the description, and does not necessarily preclude chemical interactions among the constituents of a mixture once mixed; specification of materials in ionic form implies the presence of sufficient counterions to produce electrical neutrality for the composition as a whole, and any counterions thus implicitly specified preferably are selected from among other constituents explicitly specified in ionic form, to the extent possible; otherwise such counterions may be freely selected, except for avoiding counterions that act adversely to the objects of the invention; the term "paint" and its grammatical variations includes any more specialized types of protective exterior coatings that are also known as, for example, lacquer, electropaint, shellac, top coat, base coat, color coat, and the like; and the term "mole" and its variations may be applied to ionic, chemically unstable neutral, or any other chemical species, whether actual or hypothetical, that is specified by the type(s) of atoms present and the number of each type of atom included in the unit defined, as well as to substances with well defined neutral molecules.

BRIEF SUMMARY OF THE INVENTION

The invention provides a method of cleaning paint from non-water-soluble surfaces, especially metal surfaces, comprising contacting the paint with an aqueous composition comprising a water-soluble alkoxylated aromatic alcohol such as an ethoxylated phenol or an ethoxylated benzyl alcohol which contains an aromatic ring moiety but which does not bear any alkyl substituent having more than 4 carbon atoms. In preferred embodiments, the aqueous composition is additionally comprised of a

base such as a water-soluble alkanolamine. The aqueous composition is preferably homogenous and single phase in character.

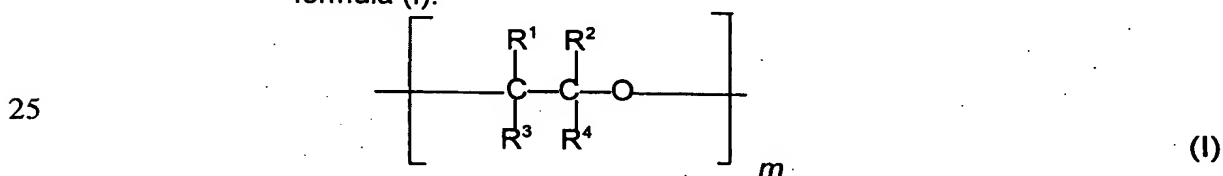
DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The present invention is particularly suitable for use in removing uncured water-borne paint from surfaces and the various embodiments described as preferred herein are preferred with respect to such end-use application. However, the invention is also useful for removing cured water-borne paint as well as solvent-borne paint, although for such applications variations from the embodiments described herein as preferred may be necessary in order to achieve optimum results.

It has been found that aqueous solutions of water-soluble alkoxyated aromatic alcohols containing oxyalkylene moieties such as oxyethylene but which do not have relatively long chain alkyl groups substituted on the aromatic ring are quite effective in removing paint residues from surfaces. Preferably, the alkoxyated aromatic alcohol component of the paint-removing solution contains an average of from about 2 to about 10 oxyethylene moieties per molecule.

The alkoxyated aromatic alcohol preferably is a non-ionic organic compound comprising, in each molecule:

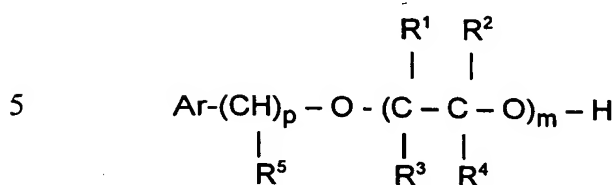
- (1) an aromatic ring moiety, wherein said aromatic ring moiety does not bear any alkyl substituent containing more than 4 carbon atoms; and
- (2) a linear moiety that conforms to the immediately following general formula (I):



wherein m represents a positive integer of at least 2 and each of R^1 through R^4 , independently for each and independently from one to another of the m instances of each of R^1 through R^4 in said linear moiety, represents either a covalently bonded hydrogen atom or a covalently bonded methyl moiety. The above-mentioned linear moiety is attached to the aromatic ring moiety, preferably through an ether oxygen alone or through an oxymethylene ($-\text{CH}_2 - \text{O} -$) moiety. The end of the linear moiety which is not attached to the aromatic ring moiety is preferably hydroxyl-terminated (i.e., an OH group is present at one end of the linear moiety).

In one embodiment of the invention the water-soluble alkoxyated aromatic

alcohol component is a mixture of compounds corresponding to the general structure.



wherein m represents a positive integer which is at least about 2 on average (more preferably, at least about 3 on average) and independently is no more than about 10 on average (more preferably, no more than about 5 on average), each of R¹ through R⁴ independently from one to another of the m instances of each of R¹ through R⁴ in the same molecule, represents either a covalently bonded hydrogen atom or a covalently bonded methyl moiety, subject to the proviso that at least about 70 number % (more preferably, at least 80 number %; most preferably, at least about 90 number % of the moieties) indicated by the symbols R¹ through R⁴ in said mixture represent hydrogen atoms, Ar is a substituted or unsubstituted phenyl moiety ("unsubstituted" meaning that there are no substituents on the phenyl ring other than the oxyalkylene moieties), subject to the proviso that Ar contains no alkyl substituent containing more than 4 carbon atoms (more preferably, Ar contains no alkyl substituent containing more than 2 carbon atoms; most preferably, Ar contains no alkyl substituent containing more than 1 carbon atom), R⁵ is selected from hydrogen or methyl, and p is 0 or 1.

Representative preferred alkoxyated aromatic alcohols include triethylene glycol monophenyl ether, tetraethylene glycol monophenyl ether, pentaethylene glycol monophenyl ether, hexaethylene glycol monophenyl ether, heptaethylene glycol monophenyl ether, triethylene glycol monobenzyl ether, tetraethylene glycol monobenzyl ether, pentaethylene glycol monobenzyl ether, hexaethylene glycol monobenzyl ether, heptaethylene glycol monobenzyl ether, water-soluble ethoxylates of propylene glycol monophenyl ether (preferably, containing an average of at least 2 oxyethylene moieties per molecule), and the like and mixtures thereof. Suitable alkoxyated aromatic alcohols are available from commercial sources such as Harcross (T Det P4) and Clariant (ST-8329 and Genapol ® BA 04).

Non-exclusive examples of suitable ring moieties for part (1) of the alkoxyated aromatic alcohol molecules as described above are the rings of benzene and naphthalene. Any of the positions on these rings may be substituted with halogen or

alkyl moieties, and at least one of the positions on these rings must be substituted with a moiety that includes a linear moiety as described in part (2) above. These linear moieties are normally produced by condensing at least one alkylene oxide (e.g., ethylene oxide, propylene oxide) with a suitable compound having at least one active hydrogen (e.g., phenol, benzyl alcohol), as is generally well known in the art. Alkoxylation is preferably carried out under conditions effective to react an average of at least about two (more preferably, at least about three) moles of alkylene oxide per mole of active hydrogen in the aromatic alcohol.

At least for economy, for the alkoxyated aromatic alcohol component the following preferences apply, each independently of the others, with combinations of the preferences being still more preferred, the greater the number of the following preferences that apply simultaneously:

- there is only one ring moiety in each molecule;
- at least, with increasing preference in the order given, 50, 70, 80, 90, 95, or 99 number % of the ring moieties are phenyl rings, optionally substituted but more preferably unsubstituted, except for any substituent that contains a linear moiety according to general formula (I);
- any substituent on a ring moiety, except a substituent that contains a moiety according to general formula (I), contains not more than, with increasing preference in the order given, 4, 3, 2, or 1 carbon atoms and not more than, with increasing preference in the order given, 3, 2, 1, or 0 of any atoms except carbon and hydrogen atoms;
- at least, with increasing preference in the order given, 50, 60, 70, 75, 80, 85, 90, 95, or 99 number % of the moieties indicated by the symbols R^1 through R^4 in general formula (I) represent hydrogen atoms;
- the average number of carbon atoms in the shortest path along chemical bonds between a carbon atom that is part of a ring moiety as defined in part (A)(1) above and an oxygen atom that is either bonded directly to a moiety conforming to general formula (I) or is itself part of a moiety conforming to general formula (I) is not more than, with increasing preference in the order given, 10, 8, 6, 4, 3.0, 2.5, 2.0, 1.5, or 1.0;
- there is a ratio between the number of carbon atoms in moieties that conform to the general formula $-\text{CH}_2-\text{CH}_2-\text{O}-$ and the number of all other carbon atoms in the alkoxyated aromatic alcohol component that is at least, with

- increasing preference in the order given, 0.10:1.00, 0.20:1.00, 0.30:1.00, 0.40:1.00, 0.45:1.00, 0.50:1.00, 0.54:1.00, 0.56:1.00, 0.58:1.00, or 0.60:1.00 and independently preferably is not more than, with increasing preference in the order given, 2.00:1.00, 1.5:1.00, 1.0:1.00, 0.90:1.00, 0.85:1.00, 0.82:1.00, 0.80:1.00, 0.78:1.00, 0.76:1.00, 0.74:1.00, 0.72:1.00, or 0.70:1.00;
- where a mixture of alkoxyated aromatic alcohols is used, the number percent of molecules of the mixture for which the value of m in general formula (I) has the value of the nearest integer to the number average value of m for the mixture as a whole is at least, with increasing preference in the order given, 10, 13, 16, 18, 20, or 22 % and independently preferably is not more than, with increasing preference in the order given, 75, 60, 50, 40, 35, 30, 28, 26, or 24 %;
- the number percent of molecules of a mixture of alkoxyated aromatic alcohols for which the value of m in general formula (I) has a value that does not differ by more than 1 from the nearest integer to the number average value of m for the mixture as a whole is at least, with increasing preference in the order given, 30, 35, 40, 45, 50, 54, 57, or 60 % and independently preferably is not more than, with increasing preference in the order given, 90, 80, 73, 69, 66, 64, or 62 %; and
- the number percent of molecules of a mixture of alkoxyated aromatic alcohols for which the value of m in general formula (I) has a value that does not differ by more than 2 from the nearest integer to the number average value of m for the mixture as a whole is at least, with increasing preference in the order given, 60, 70, 75, 78, 80, 82, or 84 % and independently preferably is not more than, with increasing preference in the order given, 95, 93, 91, 89, 87, or 85 %.
- In preferred embodiments of the invention, the alkoxyated aromatic alcohol is used in combination with a water-soluble base (i.e., a substance capable of rendering the aqueous composition used as a paint removing solution alkaline). Organic as well as inorganic bases may be employed, although organic bases are generally preferred. Generally speaking, an amount of base is preferably used which is sufficient to provide a pH in the working paint-removing solution of from about 8 to about 14 (more preferably, from about 9.5 to about 11.5).

The base component as described above preferably is an alkanolamine and preferably is selected from alkanolamine molecules that jointly have the following characteristics, each of which is preferred individually and combinations of which are still

more preferred, the greater the number of individual preferences in the combination:

- the average number of amino nitrogen atoms per molecule is not more than, with increasing preference in the order given, 5, 3, 2.0, 1.8, 1.6, 1.4, 1.2, or 1.0;
- the average number of moieties other than hydrogen atoms that are directly bonded to each amino nitrogen atom is not more than, with increasing preference in the order given, 2.5, 2.0, 1.7, 1.4, 1.2, or 1.0;
- the average number of carbon atoms per amino nitrogen atom is not less than, with increasing preference in the order given, 1.5, 2.0, 2.5, 2.7, or 2.9 and independently preferably is not more than, with increasing preference in the order given, 10, 8, 6, 5.0, 4.5, 4.0, 3.8, 3.6, 3.4, 3.2, or 3.0;
- the average number of hydroxyl moieties per amino nitrogen moiety is at least, with increasing preference in the order given, 0.2, 0.4, 0.6, 0.70, 0.75, 0.80, 0.85, 0.90, 0.95, or 0.98 and independently preferably is not more than, with increasing preference in the order given, 2.5, 2.0, 1.7, 1.4, 1.2, or 1.02;
- the percent of total nitrogen atoms that are amino nitrogen atoms is at least, with increasing preference in the order given, 50, 60, 70, 80, 90, 95, or 99 %; and
- the percentage of total oxygen atoms that are part of hydroxyl moieties is at least, with increasing preference in the order given, 50, 60, 70, 80, 90, 95, or 99 %.

The single most preferred substance for the base component is 2-aminopropanol-1 (also known as monoisopropanolamine), but other suitable alkanolamines include dimethylethanolamine, diethanolamine, triethanolamine, triisopropanolamine, monoethanolamine, n-butyl diethanolamine, 2-methylaminoethanol, n-butylaminoethanol, diethylaminoethanol, 2-amino-2-methyl-1-propanol, phenyl diethanolamine, diisopropanolamine and the like. Other water-soluble amines such as alkylamines (e.g., triethylamine) and oxazolidines may also be used. Examples of suitable inorganic bases include alkali metal hydroxides, alkali metal carbonates, alkali metal silicates, alkali metal phosphates, and other basic alkali metal salts. In one embodiment of the invention, an alkanolamine is used in combination with an alkali metal silicate such as sodium silicate (preferably, at a silicate concentration in the working solution of from about 0.001 to about 0.1 weight percent).

The ratio by mass of the alkoxyated aromatic alcohol component as described above to the base component as described above in a concentrate or a working composition according to this invention preferably is (where the base is an amine) at

least, with increasing preference in the order given, 1.0:1.00, 2.0:1.00, 3.0:1.00, 4.0:1.00, 5.0:1.00, 6.0:1.00, 7.0:1.00, 7.5:1.00, 8.0:1.00, 8.5:1.00 or 8.9:1.00 and independently preferably is not more than, with increasing preference in the order given, 40:1.00, 30:1.00, 25:1.00, 20:1.00, 15:1.00, 13:1.00, 11.0:1.00, 10.5:1.00, 10.0:1.00, 9.8:1.00, 9.6:1.00, 9.4:1.00, 9.2:1.00, or 9.1:1.00. If a relatively strong inorganic base such as an alkali metal hydroxide is used, the preferred alkoxylated aromatic alcohol:base mass ratio will generally be higher.

The various components of the working water-based, paint-removing solutions of the present invention and the concentrations of such components are preferably selected such that the composition has a VOC content (as measured by EPA Method 24) of less than about 0.1 lb./gal, preferably less than about 0.08 lb./gal, and most preferably less than about 0.06 lb./gal.

In a concentrate composition according to the invention, substantial concentrations of water are economically disadvantageous, because they increase the cost of shipping the active ingredients of the concentrate from its point of manufacture to its point of use. However, this disadvantage is purely economic rather than technical and is therefore minimal if the concentration of water in a concentrate is not more than about 10 %. On the other hand, water is usually economically necessary in a working composition for actual paint removal according to the invention.

Ordinarily, components other than water, alkoxylated aromatic alcohol and base are not needed in a composition according to the invention and in such instances are preferably omitted, at least for economy. However, an additional surfactant may be needed in some instances to improve initial wetting of the paint to be removed from the substrate surface. The surfactant may be anionic, non-ionic, cationic or amphoteric in character, but preferably is a low foaming surfactant or is used in combination with a defoamer to minimize the amount of foam generated during use. Examples of suitable surfactants include alkylaryl sulfonates such as sodium xylene sulfonate, ethoxylated fatty esters and oils such as MERPOL A (available commercially from E.I. duPont de Nemours & Co.), non-ionic fluorocarbon-based surfactants such as ZONYL FSN (available from E.I. duPont de Nemours & Co.), and non-ionic ethoxylated alkylphenols such as ethoxylated octylphenol. If the water used is very "hard", meaning that it contains substantial concentrations of calcium and/or magnesium cations, a chelating agent for these ions may be needed to prevent unwanted precipitation of scums on the surfaces being cleaned. Suitable chelating agents include water-soluble compounds

containing two or more functional groups such as carboxylic acid groups, phosphoryl groups, amine groups, and/or hydroxyl groups which are arranged in suitable positions in the chelating agent molecule such that atoms in two or more functional groups are capable of complexing with a singlr calcium and/or magnesium cation. Non-limiting
5 examples of suitable chelating agents include EDTA, gluconic acid, citric acid, polyphosphonic acids, and salts thereof. In some instances for removing especially difficult paints, additional solvent may be needed and may be tolerable even if it increases the VOC content of the composition. The auxiliary solvents are preferably water-soluble and may be selected from, for example, polyalkylene glycols, glycols,
10 glycol ethers, glycol esters, glycol oligomers, aliphatic and aromatic alcohols, ethers, ketones, and the like. Corrosion inhibitors may also be present in the paint-removing compositions of the present invention.

Small amounts of alkoxyated aromatic alcohols having a relatively low degree of alkoxylation (e.g., wherein n in the aforescribed general formula is 1) may also be
15 present in the composition, but it is preferred that such amounts be minimized since such compounds are only sparingly soluble in water and undesirably increase the VOC content of the composition. Also, under at least some conditions, such compounds have surprisingly been found to be less efficient in removing paint than the more highly alkoxyated aromatic alcohols which are the subject of the present invention.

20 In a process according to the invention, contact between the solution as described above and any paint contaminated surface to be cleaned of paint may be brought about by any convenient method. Immersion and spraying are the most common methods. If the surface to be cleaned has a shape that can be readily and reasonably uniformly contacted by spraying, this method of contact is generally
25 preferred, because the mechanical force of impingement of the sprayed solution aids in efficient paint removal. On the other hand, if the surface to be cleaned has recesses or other shapes that can not readily be contacted by spraying, immersion (flooding) will generally be preferred. The solution may be agitated to help accelerate the rate of paint removal. Both methods can, of course be combined and/or varied in ways apparent to
30 those skilled in the art. The optimum values of active ingredient concentrations and temperature of the working solution depend to some extent on the method of contact and the impingement force (if any) achieved by the contact. General guidelines for spraying are given below, but in any instance, those skilled in the art will be able to determine optimum conditions by minimal experimentation.

In a working paint-removing solution, the concentration of the alkoxyated aromatic alcohol component as described above preferably is at least, with increasing preference in the order given, 0.5, 1.0, 1.3, 1.6, 1.9, 2.1, 2.3, or 2.5 % and independently preferably, at least for economy, is not more than, with increasing preference in the order given, 30, 20, 10, 8, 6.0, 5.0, 4.5, or 4.0 %. The concentration of the base component (when one or more water-soluble amines are used as the base component) preferably is at least, with increasing preference in the order given, 0.05, 0.1, 0.15, 0.20, 0.25 % and independently preferably, at least for economy, is not more than with increasing preference in the order given, 3, 2, 1, or 0.5 %. Higher concentrations within these preferences are preferred for immersion or low force spraying, while lower concentrations are satisfactory technically and are more economical for high force spraying.

Spraying pressure will normally range from 1.3 to 8.0 bars absolute pressure.

Near the lower end of this range, the temperature of the paint-removing solution preferably is at least, with increasing preference in the order given, 15, 20, 25, 30, 40, 50, 55, or 60 °C if speed of removal of the paint is important. On the other hand, if the spraying pressure is as much as 2.7 bars, there is no technical advantage to a solution temperature greater than 38 °C, because the contact time required is not substantially reduced by higher temperature, while the energy cost of the process is increased.

The compositions of the present invention are also useful for purging paint residues from automated and manual equipment such as paint sprayers and paint dip installations. Typically, the concentrate composition is introduced into a purge tank containing an amount of deionized water effective to dilute the concentrate composition to a concentration of between about 5% and about 15% by volume. The resulting working purge solution is heated to a temperature of from about 38°C to about 54°C and then circulated through the equipment to purge any residual paint from the equipment. When actually contacted with the surfaces of the equipment containing the paint residues, the use temperature of the working purge solution is typically about 26°C to about 32°C due to heat losses during circulation. To minimize waste, the used purge solution may be reconditioned (by removing paint solids through means such as filtration, settlement, coagulation or the like and/or replenishing one or more components of the purge solution) and recirculated through the equipment. Prior to and/or after circulation of the working purge solution, the equipment may be subjected to other cleaning methods such as purging with water alone or with a gas such as air

or nitrogen.

The contact time needed to effect a substantial loosening of the paint from a surface will depend on the nature and thickness of the paint, the relative activity of the components in the composition, the concentrations of such components, and the temperature of the solution, among other factors. With some paints and under some conditions, contact times of a few minutes (e.g., 2-3 minutes) may be sufficient, while with other more difficult to remove paints and with more dilute solutions or lower contact temperatures, appreciably longer contact times (e.g., up to 1 hour) may be desirable.

The invention and its benefits compared with prior art processes may be further appreciated by consideration of the following working and comparative examples, which are not to be understood as limiting the invention in any way except to whatever extent conditions used in the examples may be found in the appended claims.

TEST SUBSTRATES

Static Dwell Test Substrates and Method: Thin films of waterborne paint were applied to a glass panel and subsequently baked at 49 to 55 °C for 0.5 to 4 hours. The tested working paint-removing solutions were applied dropwise to the thus prepared test panels, which were then observed to determine the point at which the film softened or bubbled.

Spray Test Method: Thin films of waterborne paint were applied to a glass panel and subsequently baked at 49 °C for 0.5 hours. A conventional spray gun having a 1.07 millimeter fluid tip size was positioned 10 centimeters away from a thus prepared glass panel. Using a fluid pressure as noted below for a particular instance, a solid stream of liquid was directed onto the coated glass panel until a circle of baked paint with a diameter of 10.4 millimeters was completely cleaned from the panel, and the time required was recorded. (In some instances in comparative examples, such cleaning was not achieved within the maximum time allowed; any such instance is noted explicitly.) Temperatures are also specified below for each particular test.

WORKING AND COMPARATIVE EXAMPLE GROUP 1

In this group, the following concentrates were used to make the paint-removing solutions used: Comparative Concentrate C1.1 consisted of 98 % of ethylene glycol n-butyl ether and 2 % of 2-aminopropanol-1; Working Concentrate C1.2 consisted of 10 % of 2-amino-propanol-1 and 90 % of Harcross T Det P4™ ethoxylated phenol, which was reported by its supplier to have the following distribution of degrees of ethoxylation, where the number of oxyethylene units per molecule is indicated by *n*: 3.3 % of *n*=1,

or nitrogen.

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11.6 % of $n=2$, 19.9 % of $n=3$, 22.4 % of $n=4$, 18.6 % of $n=5$, 12.3 % of $n=6$, 6.7 % of $n=7$, 3.1 % of $n=8$, 1.26 % of $n=9$, balance of $n \geq 10$; Comparative Concentrate C1.3 consisted of 2-aminopropanol-1 only. These concentrates (when used) were diluted with deionized water to make the working compositions shown in Table 1. All of the test
5 substrates used in this group were prepared with the same paint, Du Pont water-based Galaxy Silver automobile paint, under the conditions noted above for spray testing.

Table 1

Con- cen- trate Used	% by Volume of Con- centrate in Work- ing Paint- Removin g Solu- tion	Spray Pres- sure, Bars Abso- lute	Cleaning Characteristics			
			Average Seconds of Spray- ing	Num- ber of Tests	% Devia- tion from the Mean, If More Than One Test	Observation of Thoroughness of Cleaning
C1.1	10	1.3	19.5	3	4.2	Clean
C1.1	5	1.3	19.3	1		Clean
C1.3	1	1.3	31	1		Film of silver flakes left on panel
None	None	1.3	60	1		20 % Removed, with a film of silver flakes left on panel
C1.2	5	1.3	14.1	1		Clean
C1.1	10	2.0	4.1	1		Clean
C1.1	5	2.0	8.0	3	9.0	Clean
C1.3	1	2.0	11.0	1		Film of silver flakes left on panel
None	None	2.0	60	1		60 % Removed, with a film of silver flakes left on panel
C1.2	5	2.0	5.1	1		Clean
C1.1	10	2.7	4.1	2	5.5	Clean
C1.1	5	2.7	6.3	1		Clean
C1.3	1	2.7	7.8	1		Film of silver flakes left on panel
None	None	2.7	23	1		90 % Removed, with a film of silver flakes left on panel
C1.2	5	2.7	3.9	1		Clean

WORKING AND COMPARATIVE EXAMPLE GROUP 2

- 5 In this group, Du Pont Galaxy Silver, BASF Red Primer, and BASF Imola R d Primer automobile paints were tested by spraying. Working Concentrate C2.1 was the same as Working Concentrate C1.2. Working Concentrate C2.2 consisted of 90 % of ethoxylated benzyl alcohol (ST-8329 from Clariant Corporation) with an average of 4 oxyethylene units per molecule and 10
- 10 % of 2-amino-propanol-1. Working Paint-Removing Solutions PRS2.1 and PRS2.2 consisted of 3.0 % by volume solutions of C1.1 and C1.2 respectively in deionized

water, and Comparative Paint-Removing Solution PRS2.3 was a solution of 0.3 % of 2-aminopropanol-1 in deionized water. All of the working solutions were maintained at 49 °C during testing. Spray pressures and test results are shown in Table 2. These results indicate that ethoxylated benzyl alcohol performs equivalently to or very slightly better than ethoxylated phenol.

Table 2

Paint	Working Paint-Removing Solution	Spray Pressure, Bars Absolute	Spraying Time, Seconds
Du Pont Galaxy Silver	PRS2.2	1.3	8.6
Du Pont Galaxy Silver	PRS2.1	1.3	9.3
Du Pont Galaxy Silver	PRS2.2	2.7	2.5
Du Pont Galaxy Silver	PRS2.1	2.7	2.6
BASF Red Primer	PRS2.2	2.7	1.62
BASF Imola Red Primer	PRS2.2	2.7	1.25
Du Pont Galaxy Silver	PRS2.3	2.7	3.5*
Du Pont Galaxy Silver	PRS2.3	1.3	15.9*

*A substantial paint film was left on the area nominally cleaned in these comparative examples.

EXAMPLE AND COMPARATIVE EXAMPLE GROUP 3

In this group, the effectiveness of various alkoxyated aromatic alcohols and comparative alternatives were determined. Unless otherwise noted, all were used to make concentrates with a 9.0:1.00 ratio between the alkoxyated aromatic alcohol component or its alternate and 2-amino-propanol-1, and the concentrates were diluted to 10 % by volume with deionized water to make the working or comparative flushing solutions. All of the working flushing solutions according to the invention were made with ethoxylated phenol, but the degree of ethoxylation was varied as shown in Table 3. The alternative substances, not according to the invention, are identified in Table 3 by the following abbreviations: A1 = Emphos™ TS-211 ethoxylated phenol phosphate ester; A2 = sodium xylene sulfonate; A3 = ethylene glycol mono-*n*-butyl ether; A4 = ethylene glycol mono-*n*-butyl ether, but with a mixing ratio to 2-amino-propanol-1 of 49:1.00 instead of 9.0:1.00;

and A5 = 2-amino-propanol-1. The paints tested, which were all commercially available water-borne automobile paints, are identified in Table 3 by the following abbreviations: P1 = PPG Silver; P2 = PPG White; P3 = PPG Red; P4 = PPG Blue; P5 = BASF Silver; and P6 = Du Pont Galaxy Silver. Three drops of the flushing solution being tested were applied to the test substrates prepared for static dwell testing as described above. Baking condition B1 was 53 °C for 4 hours; baking condition B2 was 49 °C for 0.5 hour. The following abbreviations were used to indicate the effect on the paint film if it did not dissolve: S,ns = Softened, no stripping or dissolution; Nd = no dissolution. The results are shown in Table 3 and indicate that the paint-removing solutions according to the invention were more effective overall than any of the comparative paint-removing solutions tested and have lower VOC than any of the comparative paint-removing solutions A3 through A5 that have reasonably close stripping ability for some of the paints tested. The results also indicate that the paint removing performance of solutions containing ethoxylated phenol with an average of 4 oxyethylene moieties per molecule was in most instances equivalent or superior to that of solutions containing ethoxylated phenol with an average of only 1 oxyethylene moiety per molecule. This was surprising since it had been expected that the ability of the alkoxylated phenol to loosen the paint film would decrease as the degree of ethoxylation increased. The use of ethoxylated phenols containing a higher degree of ethoxylation is also advantageous since such materials have greater water solubility and lower VOC content.

Table 3

Paint and Baking Conditions	Time in Seconds to Bubble, Significantly Soften, or Dissolve, with:								
	Ethoxylated Aromatic Alcohol, Average Oxyethylene Moieties per Molecule				Alternative to Ethoxylated Aromatic Alcohol				
	1	4	6	9	A1	A2	A3	A4	A5
P1 B1	107	24	28	34	120 S,ns	120 S,ns	35	120 S,ns	41
P2 B1	21	14.6	18.9	17.2	120 S,ns	120 S,ns	13	120	14.6
P3 B1	26	32	40	41	120 S,ns	120 S,ns	38	120	40
P4 B1	No test	14.6	16.7	17.4	120 S,ns	120 S,ns	No test	No test	21
P5 B2	29	15	22	29	120 S,ns	120 S,ns	24	24	24 Nd
P1 B2	15	12	16.5	29	20 Nd	24 Nd	24	24	24 Nd
P6 B2	22	16	26	37	120 S,ns	120 S,ns	10	21	120 S,ns

EXAMPLE AND COMPARATIVE EXAMPLE GROUP 4

In this group, a variety of ethoxylated phenols and other materials were investigated for paint removal by spraying, with the paint-removing solution at normal room temperature (about 22 °C). The paint used was Du Pont Galaxy Silver, which had been baked at 49 °C for 0.5 hour before being tested. Spray pressure was also varied.

Each tested material was mixed in a ratio of 9.0:1.00 with 2-amino-propanol-1 to form a concentrate, except that for A 11, the ratio was 49:1.00. Working paint-removing solutions were made by diluting a concentrate with deionized water to a concentration of 5 % by volume of the concentrate in the working paint-removing solution. The following alternatives for alkoxylated aromatic alcohols in accordance with the invention were used, with short identifiers used in Table 4: A6 = Triton™ X-45 ethoxylated octyl phenol surfactant; A7 = Tergitol™ NP-9 ethoxylated nonyl phenol surfactant; A8 = Neodol™ R1-5 ethoxylated alcohol surfactant; A9 = Ethomeen™ C25 ethoxylated amin surfactant; A10 = Merpol™ A ethoxylated phosphate surfactant; and A11 = Ethylen glycol mono-*n*-butyl ether. Additional specific conditions and results are shown in Table 4. Again, there was general superiority of the examples according to the invention over the comparative examples in cleaning effectiveness, reduced VOC content, or both.

Table 4

Spray Pressure, Bars Absolute	Time in Seconds to Clear (Unless Otherwise Noted)* a Circle with a Diameter of 10.4 Millimeters with Flushing Solution Containing:								
	Alkoxylated Aromatic Alcohol, Average Oxyethylene Moieties per Molecule			Alternative to Alkoxylated Aromatic Alcohol					
	4	6	9	A6	A7	A8	A9	A10	A11
1.30	26	40	40	40 Nec	40 Nec	40 Nec	40 Nec	40 30%	25
2.7	6	13	20	40 50%	40 40%	40 10%	25	40 30%	5.6

*A percentage after the number of seconds indicates the approximate % of the surface that was actually cleaned when this was not all of the surface; "Nec" means "No effective cleaning."

EXAMPLE AND COMPARATIVE EXAMPLE GROUP 5

In this group the concentration and spray pressure were the primary independent variables. All of the examples according to the invention used a concentrate that consisted of 90 % of Harcross T-Det P-4™ ethoxylated phenol and 10 % of 2-aminopropanol-1. The nature of the working solution in the comparative examples and other details and results are given in Table 5 below. The test panels were prepared in the same manner as for Group 4 and with the same paint, and the paint removing solutions were maintained at 17 °C during the spraying. At the same concentration, a paint-removing solution according to the invention was superior to an example of current commercially preferred paint-removing solutions for this application.

Table 5

Con- cen- trate Used	% by Vol- ume of Concen- trate in Working Flushing Solution	Spray Pressure, Bars Ab- solute	Cleaning Characteristics			
			Average Seconds of Spray- ing	Num- ber of Tests	% Devia- tion from the Mean, If More Than One Test	Observation of Thoroughness of Cleaning
Ac- cording to the In- vention	5.0	1.3	21	3	2.3	Completely clean
	5.0	2.7	5.1	1		Completely clean
	4.0	1.3	25	2	4.0	Completely clean
	4.0	2.7	5.4	1		Completely clean
	3.0	1.3	37	2	1.9	Completely clean
	3.0	2.7	6.7	2	3.0	Completely clean
	2.0	1.3	50	1		Completely clean
	2.0	2.7	8.7	2	3.1	Completely clean
	1.3	1.3	58	1		Completely clean
	1.3	2.7	14	1		Completely clean
None	None	1.3	120	1		No observable cleaning effect
	None	2.7	120	1		No observable cleaning effect
2- Amino- prop- anol-1	0.50	1.3	120	1		No observable cleaning effect
	1.33	2.7	26	1		Some of the paint was removed, but at least a thin layer was left over the entire sprayed area
98 % of eth- ylene glycol mono- n-butyl ether + 2 % of 2- amino- prop- anol-1	10	1.3	25	2	2.9	Completely clean
	10	2.7	4.9	2	5.2	Completely clean
	5.0	1.3	28	1		Completely clean
	5.0	2.7	8.2	1		Completely clean
	4.0	1.3	32	1		Some of the paint was removed, but at least a thin layer was left over the entire sprayed area
	4.0	2.7	13.4	1		Some of the paint was removed, but at least a thin layer was left over the entire sprayed area
	3.0	1.3	40	1		Only 30 % of the paint was removed, and at least a thin layer was left over the entire sprayed area
	3.0	2.7	20	1		Some of the paint was removed, but at least a thin layer was left over the entire sprayed area
	2.0	1.3	40	1		No observable cleaning effect
	2.0	2.7	34	1		Some of the paint was removed, but at least a thin layer was left over the entire sprayed area